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The coefficients for second harmonic generation (SHG) for the 2-methyl 4-nitroaniline/poly(methyl methacrylate) guest/host system were measured as a function of the NLO chromophore concentration and of the poling field strength. The orientational order parameters (OP) were calculated from the SHG coefficients. The OP's were found to depend on the NLO chromophore concentration. The concentration dependence was associated with Kirkwood's g-factor describing the orientational pair correlation. The ratio of order parameters L_{33}/L_{31} measured in the weak poling field condition is 3, and independent of the NLO chromophore concentration. This is in agreement with the result of a recent calculation.

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**Dipolar Interaction Assisted Effects on
Second Harmonic Generation**

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Abstract

Measurements of the second order nonlinear susceptibility by second harmonic generation (SHG) of the 2-methyl 4-nitro aniline/ poly(methyl methacrylate) guest/host system were performed as a function of the nonlinear optical (NLO) chromophore concentration and the poling field strength. The orientational order parameters (OP) were calculated from the SHG coefficients. The OPs were found to depend on the NLO chromophore concentration. The concentration dependence of the OP was described in terms of Kirkwood's g-factor associated with the orientational pair correlation. The ratio of order parameters (L_{33}/L_{31}), measured in the weak poling field condition, was 3. It was found to be independent of the NLO chromophore concentration, in agreement with the result of a recent calculation. The usual local field factor, derived without considering orientational pair correlations, was shown to be inadequate. The static dielectric constant of the guest/host system was extracted from the order parameter, using the Kirkwood-Frölich theory of dielectrics.

I. Introduction

Organic molecules, with a conjugated π -electron system terminated by donor and acceptor groups, are known to exhibit a large second order hyperpolarizability.¹ Polymer systems containing these molecules can be made to produce a large second order nonlinear optical (NLO) effect, such as the second harmonic generation. The most common method employed to obtain a high second order NLO effect in the polymer system is by electric field poling. In order to orient the NLO chromophore, the polymer containing the nonlinear optical molecules is processed as a film which is heated above its glass transition temperature (T_g) in the presence of an electric field. The material is then cooled below T_g to lock the orientation in place before the field is removed. This process breaks down the isotropic symmetry of the amorphous polymer and freezes the electric dipoles in the noncentrosymmetric order.

The fundamental second order NLO effect in the polymer lies in the existence of the orientational order parameter (OP), which is induced by the external poling field E_p . When the OP vanishes, the second order NLO effect also vanishes. To maximize the NLO effect, it is important to understand the behavior of the orientational OP connected with the effect of the poling process. The dependence of the NLO chromophore concentration of OP is also important.

The usual theoretical description of the effect of the electric field poling is based on the independent dipole orientation model.² In this model, the order parameters are simply given by the Langevin function of order n , $L_n(a)$, where $a = f_o \mu E_p / kT$, f_o is the local field factor associated with the poling field E_p , μ is the dipole moment of the NLO chromophore and T is the poling temperature. In this description, the Onsager model is invoked to describe the local field correction associated with the poling field. The effect due to orientational correlation is ignored. One consequence of the independent dipole orientation

approach is that the OP, associated with the second order macroscopic susceptibility, is practically independent of the concentration of the NLO chromophores. This result disagrees with the result of the electro-optical measurement in the guest/host system.³ A recent calculation, based on a statistical mechanics approach, has shown that the OP is generally a complex function of the chromophore concentration ρ .⁴ In the specific case of the dipole-dipole interaction mechanism, the complex concentration dependence of the OP can be expressed in terms of Kirkwood's g-factor. This factor is associated with the orientational pair correlation of the interacting dipoles, which is related to the dielectric constant of the medium.⁵

In this paper, we report the study of the OP as a function of the NLO chromophore concentration in the 2-methyl 4-nitro aniline/poly(methyl methacrylate), MNA/PMMA, (guest/host) system. The OP is calculated from the second order susceptibility, $\chi^{(2)}(-2\omega; \omega, \omega)$, obtained from measurements of the intensities of the second harmonic generation at different polarizations. We compare the experimentally obtained OPs with those calculated from the independent dipole orientation model, and with the model containing the orientation pair correlation effect.

II. Experimental

Different amounts of MNA and PMMA were dissolved in chloroform to form solutions of various chromophore concentration. The amount of chloroform in each solution was adjusted to give the desired viscosity suitable for spin coating. The solutions were filtered to remove undissolved particulate. Films were prepared by spin coating the polymer solution on the soda lime glass slides, which were pre-coated with 300Å SiO₂ and 250Å ITO. A similar ITO coated soda lime glass slide was then placed on top of the polymer/ITO glass slide to form a sandwich configuration for electrode poling. The NLO polymer/ITO sample

assembly was placed in a vacuum oven at 25°C for more than 24 hours in order to remove the solvent used in spin coating. The technique of corona poling was also used to obtain higher orientation of the chromophores. This technique is similar to that employed by Eich et al.⁶

The glass transition temperatures of the samples were determined by a DSC (Perkin Elmer Delta series). The refractive indices of the samples were determined by a prism coupler (Matricon) modified for the multiple wavelength operation.⁷ The prism coupler is operated in accordance with the optical waveguide principle where the polymer film served as the propagation layer in the slab waveguide configuration. The refractive index, n , dispersion for the MNA/PMMA system is shown in Fig. 1, which can be fitted to the equation

$$n(\lambda) = 1.4957 + \frac{7743.6311}{\lambda^2 - 5177.4245} \quad (1)$$

where λ is the wavelength in nm. Also included in Fig. 1 is the MNA concentration dependence of n , measured at the optical wavelength equal to 632.8 nm. Absorption spectra were recorded with an HP 8452A diode array UV-VIS spectrometer. The intensity of the absorption spectrum was used to calibrate the chromophore concentration of the sample.

The second harmonic generation (SHG) experimental setup is shown in Fig. 2. A Nd:YAG laser (Spectra-Physics GCR-11, $\lambda = 1.06 \mu\text{m}$, Q-switched at 10 Hz, 250 mJ per pulse) was used to measure the second order nonlinear susceptibility of the poled MNA/PMMA film, which was mounted on a computer controlled goniometer stage. The film mounted on the ITO electrodes was heated in a heating/cooling device on the goniometer stage. Either the electrode poling or the corona poling technique was employed during the optical measurement. The fundamental wave was blocked by a short-pass filter.

The second harmonic signal, obtained in transmission, was selected from a monochromator. It was detected by a photomultiplier tube, followed by a pre-amplifier, and finally averaged by a boxcar integrator (EG & G 4422). The boxcar output was interfaced to a PC. The Maker fringes of a single crystal quartz plate ($d_{11} = 0.5 \text{ pm/V}$) were used as reference to determine the incident laser power employed in the measurement of the second order susceptibilities of the samples.

Results and Discussion

Shown in Fig. 3 are the boxcar output signals plotted versus the goniometer rotation angle ϕ for the MNA/PMMA film at two different polarizations of the input beam. Here ϕ is the angle between the propagation direction and the normal to the film surface. For an isotropic film, subject to a poling electric field in the direction perpendicular to the film surface, the transmitted second harmonic power density $I_{2\omega}$ for a material with a nonlinear optical coefficient $d = \frac{1}{2} \chi^{(2)}(-2\omega; \omega, \omega)$ is given by ⁸

$$I_{2\omega} = \frac{(8\pi)^3}{c} t_0^4 I_\omega^2 P^2(\phi) d^2 \left[\frac{T_{2\omega}(\phi)}{(n_\omega^2 - n_{2\omega})^2} \right] \sin^2 \left(\frac{\pi \ell}{2\ell_c} \right) \quad (2)$$

where c is the velocity of light in vacuum; I_ω is the power density of the fundamental beam inside the medium; $P(\phi)$ is the projection factor, which depends on the polarization of the incident beam and the direction of the induced nonlinear polarization. t_0 is the transmission coefficient of the second harmonic light through the substrate. $T_{2\omega}(\phi)$ is the transmission factor, which depends on the polarization of the incident beam, the incidence angle ϕ , as well as n the refractive index of the material at the fundamental (n_ω) and at second harmonic ($n_{2\omega}$) frequencies. The $T_{2\omega}(\phi)$ transmission coefficient suitable for the sandwich configuration is:

$$T_{2\omega}(\phi) = \frac{2n_{2\omega} \cos \phi'_{2\omega} (n_0 \cos \phi + n_\omega \cos \phi'_\omega) (n_\omega \cos \phi'_\omega + n_{2\omega} \cos \phi'_{2\omega})}{(n_{2\omega} \cos \phi'_{2\omega} + n_0 \cos \phi)^2 (n_{2\omega} \cos \phi'_{2\omega} + n_\omega \cos \phi)} \quad (3)$$

for the nonlinear polarization perpendicular to the plane of incidence, and

$$T_{2\omega}(\phi) = \frac{2n_{2\omega} \cos \phi'_{2\omega} (n_\omega \cos \phi + n_0 \cos \phi'_\omega) (n_{2\omega} \cos \phi'_\omega + n_\omega \cos \phi'_{2\omega})}{(n_{2\omega} \cos \phi + n_0 \cos \phi)^3} \quad (4)$$

for the nonlinear polarization in the plane of incidence. Here n_0 is the refractive index of the substrate. The quantity ℓ_c is the correlation length. It is given by: $\ell_c = \lambda/4 |n_\omega \cos \phi'_\omega - n_{2\omega} \cos \phi'_{2\omega}|$, where ϕ'_ω and $\phi'_{2\omega}$ are the angles of refraction of the fundamental and the second harmonic beams in the NLO medium, respectively. They are related to the incident angle ϕ by Snell's law as $\sin \phi'_\omega = \sin \phi / n_\omega$ and $\sin \phi'_{2\omega} = \sin \phi / n_{2\omega}$. In Eqs. (3) and (4), we follow ref. 8 by designating the quantities inside the NLO medium by a prime.

We obtained the nonlinear optical coefficients by fitting the measured intensities in both the p and s polarizations versus angle (ϕ) data to Eqs. (2-4). We used the Maker fringes of the quartz plate to determine the incident intensity of the fundamental beam needed in Eq. (2). Other data also needed for the fit were the film thickness ℓ and the refractive indices n_ω and $n_{2\omega}$. Those were determined by waveguide experiments involving the use of a prism coupler. The results are given in Fig. 1 and also Eq. (1). The fitted curves from the experimental results, at s and p polarizations for 10 wt% sample, are shown in Fig. 3. The steady state values $\chi_{33}^{(2)}$ and $\chi_{31}^{(2)}$, obtained from fitting the SHG intensities of various MNA/PMMA samples at 90°C with the poling field $E_p = 2 \times 10^6$ V/cm, are shown in Table I for several MNA concentrations. The $\chi_{31}^{(2)}$ value was first determined from the SHG intensity vs. ϕ data with the fundamental beam at the s-polarization. The result was then used in the analysis of the SHG intensity vs. ϕ data set obtained with the p-polarization to obtain the $\chi_{33}^{(2)}$ value. One notes for the contact electrode poled films,

the average value of the $\chi_{33}^{(2)}/\chi_{31}^{(2)}$ ratios is equal to 3.16 ± 0.30 .

The NLO coefficients are related to the orientational order parameters by^{1,2}

$$\chi_{33}^{(2)} = \rho \beta f_{2\omega} f_{\omega}^2 \langle \cos^3 \theta_1 \rangle \quad (5)$$

and

$$\chi_{31}^{(2)} = \rho \beta f_{2\omega} f_{\omega}^2 (\langle \cos \theta_1 \rangle - \langle \cos^3 \theta_1 \rangle)/2 \quad (6)$$

where ρ is the number density of the chromophores and β is the dominant component of the hyperpolarizability tensor along the molecular principal axis. The subscript 1, associated with θ_1 , refers to the representative NLO chromophore 1. In the Lorentz model, the local field factors $f_{2\omega}$ and f_{ω} are given by $f_{2\omega} = (n_{2\omega}^2 + 2)/3$ and $f_{\omega} = (n_{\omega}^2 + 2)/3$, respectively. The orientational order parameters for $\chi_{33}^{(2)}$ and $\chi_{31}^{(2)}$ are thus $L_{33} = \langle \cos^3 \theta_1 \rangle$, and $L_{31} = \frac{1}{2} [\langle \cos \theta_1 \rangle - \langle \cos^3 \theta_1 \rangle]$, respectively. Here the angular brackets denote the ensemble average. Both L_{33} and L_{31} are functions of the poling parameter a , given previously in the Introduction Section.

Using the refractive index dispersion data, measured from films containing different MNA concentrations, we calculated the Lorentz-Lorentz local field factors $f_{2\omega}$ and f_{ω} . The results are then substituted into Eqs. (5) and (6) to obtain the orientational order parameters (OP) from the experimentally determined $\chi_{31}^{(2)}$ and $\chi_{33}^{(2)}$ SHG coefficients. The results for OP, obtained from $\chi_{31}^{(2)}$, are plotted versus the MNA concentration in Fig. 4. We include the β value in the right vertical axis of the plot as there may exist a significant uncertainty in β by the SHG method and the value of the order parameter depends on the accurate value of β . However, if a reliable β value is available, the OP is readily obtained by dividing the ordinate by the β value. One notes that over the entire concentration range, with number density, ρ , varying from 0 to about 6×10^{20} chromophores/cm³, the order

parameter increases by a factor of 1.53 (the value of βL_{31} increases from 12.36 to $18.9 \times 10^{-40} \text{ m}^4/\text{V}$). By extrapolating the OP value to zero MNA concentration, we obtain a finite intercept. The intercept is equal to $\frac{\mu E_p f_0}{15kT}$, where f_0 is the local field factor due to PMMA

host. From this result, we can calculate E_p and compare it with the poling field actually used. In the case of corona poling, where the poling field strength cannot be measured directly, we can determine E_p from the intercept.

The order parameter $L_{31}(a)$ can be written in terms of the ensemble averages of the Legendre polynomials $\langle P_1(\cos \theta_1) \rangle$ and $\langle P_3(\cos \theta_1) \rangle$ by

$$L_{31}(a) = \frac{1}{2}(\langle P_1 \rangle - \langle P_3 \rangle) \quad (7)$$

where for brevity we have not written out the argument $\cos \theta_1$ in the Legendre polynomials. For systems with the random orientation of the electric dipoles, $L_{31}(a)$ is zero because both $\langle P_1 \rangle$ and $\langle P_3 \rangle$ vanish. On the other hand, when the dipoles are completely oriented, we have $\langle P_1 \rangle$ and $\langle P_3 \rangle = 1$; again we obtain $L_{31}(a) = 0$. Thus, if both $\langle P_1 \rangle$ and $\langle P_3 \rangle$ contribute to $L_{31}(a)$, we expect the order parameter $L_{31}(a)$ to increase from zero to maximum value and then decrease to zero. In the independent dipole orientation model, the maximum value for $L_{31}(a)$ is about equal to 0.1 (see Fig. 4). For a chromophore with a permanent dipole moment of 5 debye subject to a field of $6.7 \times 10^6 \text{ V/cm}$. The order parameter, obtained from this experiment, is greater than 0.1. Furthermore, for a system with the concentration of NLO molecules equal to $5 \times 10^{20} \text{ molecules/cm}^3$, the dipole-dipole interaction energy is about $2.0 \times 10^{-14} \text{ erg}$, which is about equal to the dipole-electric field interaction energy ($1.67 \times 10^{-14} \text{ erg}$). Therefore, we do not expect the independent dipole orientation model to give an accurate description of the order parameter $L_{31}(a)$. By

including the orientational correlation one will obtain the L_{31} value to be greater than 0.1. We have recently shown in a theoretical paper that in the weak field approximation, only the $\langle P_1 \rangle$ term in Eq. (7) contributes to $L_{31}(a)$, the $\langle P_3 \rangle$ term is not excited by the electromagnetic radiation. This is irrespective of the nature of the anisotropic intermolecular potential that induces the orientational pair correlation between dipoles.⁴ As a result, we have $\chi_{33}^{(2)}/\chi_{31}^{(2)} = 3.0$, independent of the specific nature of the anisotropic interaction, provided that the condition $a \ll 1$ remains valid.

To show that our experimental results can be interpreted under the weak field approximation, we studied the SHG intensity as a function of the poling field strength. Shown in Fig. 5 is the plot of the SHG signal I_{SHG} as a function of E_p . In the region of 80-125 V/ μm range, I_{SHG} appears to vary with the poling field as E_p^2 . In the weak poling field approximation, the SHG signal is proportion to E_p^2 . This indicates that in the present poling field range the weak field approximation (i.e. $a \ll 1$) used for data analysis is justified.

This result is corroborated by the fact that the experimentally determined ratio $\chi_{33}^{(2)}/\chi_{31}^{(2)} = 3.16 \pm 0.3$ (Table I). The result of the concentration dependence of the order parameter, as shown in Fig. 4, strongly suggests that it is due to anisotropic intermolecular interaction. As mentioned, the anisotropic intermolecular interaction only affects the $\langle P_1 \rangle$ term and not $\langle P_3 \rangle$.

As shown in ref. 4, although any type of orientational dependent intermolecular potentials (whether it arises from short- or from long-range interactions) can affect the polar order initially induced by the external electric field, due to its long interaction range, the dipole-dipole interaction potential makes the most important contribution⁹ to the orientational pair correlation (OPC). In ref. 4, it has been shown that the dipole-dipole interaction mechanism affects only the order parameter $\langle P_1 \rangle$. Furthermore, by including the dipole-dipole interaction in the calculation of the orientational pair correlation effect,

one finds that the order parameter $L_{31}(a)$ is given by

$$L_{31}(a) = a(1 + \rho G_{\Delta})/15 \quad (8)$$

where G_{Δ} is the cluster integral associated with the solution of the molecular pair correlation function, due to the combined effect of the dipole-dipole interaction potential and a short range isotropic intermolecular potential.⁵ Since the cluster integral may either be positive or negative, the orientational order parameter, initially induced by the external field, will either be enhanced or decreased, depending on the nature of the dipolar ordering.

To show that the concentration dependent part of the OP shown in Fig. 4 is indeed due in part to the effect of dipole-dipole interaction, we infer from theory of the polar liquid, where it is known that G_{Δ} is related to the Kirkwood's g-factor by⁵

$$\rho G_{\Delta} = g_K - 1 \quad (9)$$

where g_K is the Kirkwood's g-factor defined by¹⁰

$$g_K = \frac{\langle \underline{M} \rangle^2}{N \mu^2} \quad (10)$$

where \underline{M} is the total dipole moment of the sample; N is the total number of the dipole moments.

As a result, we can write the order parameter as

$$L_{31}(a) = a g_K / 15 \quad (11)$$

We may evaluate g_K using Kirkwood-Fröhlich's dielectric theory¹¹ as

$$g_K = \frac{(\epsilon - n^2)(2\epsilon + n^2)kT}{4\pi \rho [(n^2 + 2)/3]^2 \mu^2} \quad (12)$$

Since the dielectric constants of the MNA/PMMA system is not available, we used the

experimentally obtained order parameter L_{31} , taking $\beta = 69.9 \times 10^{-40} \text{ m}^4/\text{V}$, to calculate the dielectric constant, with the help of Eqs. (11) and (12). The calculated ϵ , as a function of MNA concentration, is shown in Table I. Over the range of the MNA concentration studied, the dielectric constant of the MNA/PMMA system appears to increase linearly with increasing MNA concentration.

The dielectric constants ϵ , calculated from the order parameter, are reasonable. The dielectric constant of PMMA at room temperature is 3.6, but it increases rapidly with increasing temperature, reaching 6.2 in the vicinity of its glass transition temperature near 100°C .¹² The dielectric constant obtained from the MNA/PMMA mixture at 2 wt% MNA concentration, was 5.06. This is satisfactory because the SHG experiment is carried out at 90°C . Upon increasing MNA concentration, ϵ appears to increase rapidly and is equal to 15.94 at 14 wt%.

The static dielectric constant of MNA at room temperature is equal to 3.2^1 , but its value at 90° is not known. As is well-known, the dielectric constant of a mixture is not an additive property of the dielectric constants of its constituents. However, for a homogenous mixture, it can be shown that, to the accuracy of second order, the cubic root of the dielectric constant is additive.¹³ Namely,

$$\epsilon_{\text{mix}}^{1/3} = \phi_1 \epsilon_1^{1/3} + \phi_2 \epsilon_2^{1/3} \quad (13)$$

where ϕ_1 and ϕ_2 are the volume fraction of component 1 and 2 in the mixture, respectively. While in principle it is possible to obtain the dielectric constant of MNA from the ϵ values given in Table I using Eq. (13). Considerable inherent experimental uncertainty involved in obtaining the order parameter from the SHG experiment will render the ϵ value inaccurate. However, the result of the dielectric constant obtained is consistent with Eq.(13), and the result is sufficient to show the importance of the orientational pair correlation effect in

SHG.

Finally, we should remark that unreasonable values of the dielectric constant (e.g. negative value) are obtained if the conventional Onsager local field factor is used to fit the experimental data. We also show, in Fig. 4, the order parameter calculated on the basis of the Onsager local field factor using the dielectric constants given in Table I. The calculated OP does not reflect the concentration dependence. The Onsager local field factor has not included the effect of orientational pair correlation; unless a rather drastic concentration dependence of the static dielectric constant of the mixture is assumed, it would not describe the behavior of the orientational parameter.

In this work we have shown:

- (1) The importance of the orientational pair correlation effect in the electric field induced SHG experiment for the guest/host system.
- (2) The Onsager theory of the local field factor is inadequate of interpreting the concentration dependence of the order parameter associated with SHG.
- (3) The concentration dependence of the orientational order parameter can be accounted for by using the Frölich theory of the Kirkwood's g-factor.

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Figure Captions

- Figure 1** The refractive index, n , of 12 wt% MNA/PMMA plotted as function of optical wavelength. The MNA concentration dependence of n at $\lambda = 632.8$ nm is also shown.
- Figure 2** The second harmonic generation (SHG) experimental set up. Symbols R and S refer to reference and sample, respectively. PC is personal computer and PMT is photomultiplier tube. SHC is second harmonic crystal. The other notations are self-explanatory.
- Figure 3** The dot points represent transmitted SHG intensity processed by the boxcar integrator, plotted versus the goniometer rotation angle, ϕ , for the 10 wt% MNA/PMMA film. This data was obtained at the S and P polarizations of the input beam at $1.06 \mu\text{m}$. The theoretical fitting results for the intensity versus angle, calculated by Eq. (2), is shown by the solid curves.
- Figure 4** The orientational order parameter (OP) obtained from $\chi_{31}^{(2)}$ plotted versus MNA concentration.
- Figure 5** The transmitted SHG intensity plotted as a function of the poling field.

Table I

Experimentally obtained Second Order nonlinear susceptibility and dielectric constant of the MNA/PMMA system as a function of the MNA concentration by SHG.

wt%	2	5	8	10	14
$\chi_{31}^{(2)}$ (pm/V)	0.73	0.71	1.33	1.49	1.83
$\chi_{33}^{(2)}$ (pm/V)	2.19	2.38	4.44	4.57	5.54
$\chi_{33}^{(2)}/\chi_{31}^{(2)}$	3.01	3.35	3.34	3.07	3.03
ϵ	5.06	5.30	8.11	10.77	15.94